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(54) Title: LIGHT-DUTY LIQUID DISHWASHING DETERGENT COMPOSITIONS WHICH HAVE DESIRABLE LOW TEMPERATURE STABILITY AND DESIRABLE GREASY SOIL REMOVAL AND SUDSING CHARACTERISTICS					
(57) Abstract					
<p>Disclosed are light-duty liquid dishwashing detergent compositions that are especially useful for the manual washing of soiled dishware. Such compositions essentially contain relatively high levels of a lightly ethoxylated alkyl ether sulfate-based anionic surfactant, a nonionic surfactant component, a suds booster which is preferably an amine oxide, and an aqueous liquid carrier. Such compositions exhibit a desirable combination of good grease removal performance, high sudsing and especially beneficial low temperature phase stability. Thickened compositions of this type are also disclosed.</p>					

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**LIGHT-DUTY LIQUID DISHWASHING
DETERGENT COMPOSITIONS WHICH HAVE DESIRABLE
LOW TEMPERATURE STABILITY AND DESIRABLE GREASY SOIL
REMOVAL AND SUDSING CHARACTERISTICS**

TECHNICAL FIELD

The present invention relates to liquid dishwashing detergent compositions suitable for use in manual dishwashing operations. These compositions contain certain detergent surfactants, suds boosters and other adjuvants which in combination serve to impart desirable low temperature stability as well as consumer preferred greasy soil cleaning and sudsing characteristics to such dishwashing detergent products.

BACKGROUND OF THE INVENTION

Light-duty liquid (LDL) detergent compositions useful for manual dishwashing are well known in the art. Such products are generally formulated to provide a number of widely diverse performance and aesthetics properties and characteristics. First and foremost, liquid or gel dishwashing products must be formulated with types and amounts of surfactants and other cleaning adjuvants that will provide acceptable solubilization and removal of food soils, especially greasy soils, from dishware being cleaned with, or in aqueous solutions formed from, such products.

In addition to being suitable for cleaning dishware, LDL compositions will also desirably possess other attributes that enhance the aesthetics or consumer perception of the effectiveness of the manual dishwashing operation. Thus, useful hand dishwashing liquids should also employ materials that enhance the sudsing characteristics of the wash solutions formed from such products. Sudsing performance entails both the production of a suitable amount of suds in the wash water initially, as well as the formation of suds which last well into the dishwashing process.

Finally, LDL compositions in the form of consumer dishwashing products must exhibit sufficient physical stability to withstand conditions that such products may encounter during the course of commercial trade. Thus, such products should maintain their physical integrity during shipping and storing, which can include exposure of the products to extremes of heat and cold (including subfreezing

temperatures) as well as to prolonged periods of shipping and storage before such products are used.

Formulation of LDL products having all of the requisite or desirable performance and stability attributes is not necessarily straightforward. Materials included in such products to provide one kind of benefit may adversely affect other characteristics of the product. Given this situation, there is a continuing need to formulate manual dishwashing liquids that provide an acceptable and desirable balance between cleaning performance, product aesthetics such as sudsing, and product stability. Accordingly, it is an object of the present invention to provide light-duty liquid dishwashing compositions which are especially effective at removing greasy food soils from dirty dishware when such compositions are used in the context of a manual dishwashing operation.

It is the further object of the present invention to realize such compositions that provide suitable and desirable sudsing performance.

It is a further object of the present invention to realize such compositions that exhibit especially desirable low temperature physical stability.

It has been found that certain selected combinations of surfactants, suds boosters, and other adjuvants can be made to provide dishwashing compositions that achieve the foregoing objectives.

SUMMARY OF THE INVENTION

The present invention relates to especially stable, aqueous light-duty liquid detergent compositions having especially desirable greasy soil removal and sudsing performance when such compositions are used to clean soiled dishware. Such compositions comprise A) from about 34% to 40% of a specific type of anionic surfactant component; B) from about 0.3% to 4.5% of a certain type of nonionic surfactant component; C) from about 4.5% to 9% of a suds booster/stabilizer; and D) from about 40% to 60% of an aqueous liquid carrier.

The anionic surfactant component essentially comprises lightly ethoxylated alkyl ether sulfates containing from about 8 to 18 carbon atoms in the alkyl group. These lightly ethoxylated alkyl ether sulfates also contain from about 0.4 to 1.6 moles of ethylene oxide per molecule.

The nonionic surfactant component can be selected from C₈₋₁₈ polyhydroxy fatty acid amides, C₈₋₁₈ alcohol ethoxylates having from about 1 to 15 moles of ethylene oxide, ethylene oxide-propylene oxide block co-polymer surfactants and combinations of these nonionic co-surfactants. The suds boosters/stabilizers utilized in the compositions herein are selected from betaine surfactants, hydroxy-free fatty

acid amides, amine oxide semipolar nonionic surfactants, C₈-22 alkylpolyglycosides and combinations of these suds boosters/stabilizers. Within the composition, the total concentration of the Component B nonionic surfactant and the Component C suds booster/stabilizer must be at least about 7%.

Preferred compositions of the present invention which exhibit especially desirable low temperature stability are those which also contain a source (from about 0.2% to 2%) of both Mg⁺⁺ and Ca⁺⁺ ions and at least 4% of a hydrotrope selected from alkali metal and calcium xylene and toluene sulfonates. Light-duty liquid detergent compositions of especially desirable low temperature stability also have a pH (10% solution) of 7.5 or less. Furthermore, in such preferred compositions, if used at all, ethoxylated alcohol nonionic surfactants will comprise no more than about 1% of the composition.

The foregoing essential components, as well as a number of additional optional ingredients, can be combined in conventional manner to form the light-duty liquid dishwashing products of this invention.

DETAILED DESCRIPTION OF THE INVENTION

The light-duty liquid dishwashing detergent compositions of the present invention contain four essential components. These components are:

- (1) a certain type of anionic surfactant;
- (2) certain nonionic surfactants;
- (3) certain suds boosters/stabilizers; and
- (4) an aqueous liquid carrier.

A wide variety of optional ingredients can also be added to compliment the performance, aesthetics and/or stability characteristics of the compositions herein.

The essential and optional components of the instant light duty liquid or gel dishwashing detergents are described in detail as follows, along with composition preparation and use. In describing the compositions of the present invention, it should be noted that the term "light-duty dishwashing detergent composition" as used herein refers to those compositions which are employed in manual (i.e. hand) dishwashing. Such compositions are generally high sudsing or foaming in nature. In describing the compositions of this invention, it should also be noted that all concentrations and ratios are on a weight basis unless otherwise specified.

Anionic Surfactant Component

The compositions herein essentially contain relatively large amounts, i.e., from about 34% to 40%, of an anionic surfactant component. More preferably the anionic surfactant component comprises from about 35% to 38% of the compositions herein.

The anionic surfactant component essentially comprises lightly ethoxylated alkyl ether sulfates. Alkyl ether sulfates are also known as alkyl polyethoxylate sulfates. These lightly ethoxylated alkyl sulfates are those which correspond to the formula:

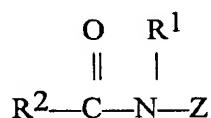


wherein R' is a C₈-C₁₈ alkyl group, n is from about 0.4 to 1.6, and M is a salt-forming cation. Preferably, R' is C₁₀₋₁₆ alkyl, n is from about 0.5 to 1.4, and M is sodium, potassium, ammonium, alkylammonium, or alkanolammonium. Most preferably, R' is C₁₂-C₁₆, n is from about 0.6 to 1.1 and M is sodium. The alkyl ether sulfates will generally be used in the form of mixtures comprising varying R' chain lengths and varying degrees of ethoxylation. Such mixtures will inevitably also contain some unethoxylated alkyl sulfate materials, i.e., surfactants of the above ethoxylated alkyl sulfate formula wherein n=0.

Nonionic Surfactants

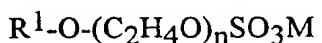
The compositions herein also essentially contain from about 0.3% to 4.5% of a certain type of nonionic surfactant component. More preferably, the nonionic surfactant component will comprise from about 0.4% to 4% of the compositions herein.

One type of nonionic surfactant which can be present in the nonionic surfactant component of the compositions herein comprises the C₈₋₁₈, preferably C₁₀₋₁₆, polyhydroxy fatty acid amides. These materials are more fully described in Pan/Gosselink; U.S Patent 5,332,528; Issued July 26, 1994, which is incorporated herein by reference. These polyhydroxy fatty acid amides have a general structure of the formula:



wherein R¹ is H, C₁-C₄ hydrocarbyl, 2-hydroxyethyl, 2-hydroxypropyl, or a mixture thereof; R² is C₈-C₁₈ hydrocarbyl; and Z is a polyhydroxylhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Examples of such surfactants include the C₁₀-C₁₈ N-methyl, or N-hydroxypropyl, glucamides. The N-propyl through N-hexyl C₁₂-C₁₆ glucamides can be used for lower sudsing performance. Polyhydroxy fatty acid amides will preferably comprise from about 1% to 5% of the compositions herein.

The nonionic surfactant component of the compositions herein may also comprise ethoxylated alcohols. Ethoxylated alcohol surfactant materials useful in the nonionic surfactant component herein are those which correspond to the general formula:



wherein R¹ is a C₈-C₁₈ alkyl group and n ranges from about 1 to 15. Preferably R¹ is an alkyl group, which may be primary or secondary, that contains from about 11 to 14 carbon atoms, more preferably from about 10 to 13 carbon atoms. Preferably the ethoxylated fatty alcohols will contain from about 2 to 12 ethylene oxide moieties per molecule, more preferably from about 6 to 12 ethylene oxide moieties per molecule. The ethoxylated fatty alcohol nonionic co-surfactant will frequently have a hydrophilic-lipophilic balance (HLB) which ranges from about 6 to 15, most preferably from about 10 to 15.

Examples of fatty alcohol ethoxylates useful as the nonionic co-surfactant component of the compositions herein will include those which are made from alcohols of 12 to 15 carbon atoms and which contain about 7 moles of ethylene oxide. Such materials have been commercially marketed under the tradenames Neodol 25-7 and Neodol 23-6.5 by Shell Chemical Company. Other useful Neodols include Neodol 1-5, ethoxylated fatty alcohol averaging 11 carbon atoms in its alkyl chain with about 5 moles of ethylene oxide; Neodol 23-9, an ethoxylated primary C₁₂-C₁₃ alcohol having about 9 moles of ethylene oxide and Neodol 91-10, an ethoxylated C₉-C₁₁ primary alcohol having about 10 moles of ethylene oxide. Alcohol ethoxylates of this type have also been marketed by Shell Chemical Company under the Dobanol tradename. Dobanol 91-5 is an ethoxylated C₉-C₁₁ fatty alcohol with an average of 5 moles ethylene oxide and Dobanol 25-7 is an ethoxylated C₁₂-C₁₅ fatty alcohol with an average of 7 moles of ethylene oxide per mole of fatty alcohol.

Other examples of suitable ethoxylated alcohol nonionic surfactants include Tergitol 15-S-7 and Tergitol 15-S-9, both of which are secondary alcohol ethoxylates that have been commercially marketed by Union Carbide Corporation. The former is a mixed ethoxylation product of C₁₁ to C₁₅ linear secondary alkanol with 7 moles of ethylene oxide and the latter is a similar product but with 9 moles of ethylene oxide being reacted.

Other types of alcohol ethoxylate nonionics useful in the present compositions are higher molecular weight nonionics, such as Neodol 45-11, which are similar ethylene oxide condensation products of higher fatty alcohols, with the higher fatty alcohol being of 14-15 carbon atoms and the number of ethylene oxide groups per mole being about 11. Such products have also been commercially marketed by Shell Chemical Company.

Ethoxylated alcohol nonionics can help impart useful cleaning attributes to the compositions herein. Such materials, however, can adversely affect low temperature stability of the products. If used, therefore, ethoxylated alcohol nonionics will preferably comprise no more than about 1%, e.g., from about 0.5% to 1%, by weight of the compositions herein.

Another type of nonionic surfactant suitable for use in the nonionic surfactant component herein comprises the ethylene oxide-propylene oxide block co-polymers that function as polymeric surfactants. Such block co-polymers comprise one or more groups which are hydrophobic and which contain mostly ethylene oxide moieties and one or more hydrophobic groups which contain mostly propylene oxide moieties. Such groups are attached to the residue of a compound that contained one or more hydroxy groups or amine groups. Such polymeric surfactants have a molecular weight ranging from about 400 to 60,000.

Preferred ethylene oxide-propylene oxide polymeric surfactants are those in which propylene oxide is condensed with an amine, especially a diamine, to provide a base that is then condensed with ethylene oxide. Materials of this type are marketed under the tradename Tetronic®. Similar structures wherein the ethylene diamine is replaced with a polyol such as propylene glycol are marketed under the tradename "Pluronic®". Preferred ethylene oxide-propylene oxide (EO-PO) polymeric surfactants have an HLB which ranges from about 4 to 30, more preferably about 10 to 20.

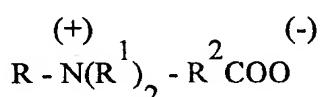
The ethylene oxide-propylene oxide block co-polymers used herein are described in greater detail in Pancheri/Mao; U.S. Patent 5,167,872; Issued December 2, 1992. This patent is incorporated herein by reference.

Ethylene oxide-propylene oxide block co-polymers will frequently be present to the extent of from about 0.1% to 1% of the compositions herein. More preferably, these polymeric surfactant materials will comprise from about 0.2% to 0.8% of the compositions herein.

Suds Boosters/Stabilizers

The compositions herein further include from about 4.5% to 9%, preferably from about 5% to 8%, of a suds booster or stabilizer component such as betaine surfactants, hydroxy-free fatty acid amides, amine oxide semi-polar nonionic surfactants, and C₈-22 alkyl polyglycosides. Combinations of these suds boosters/stabilizers can also be used.

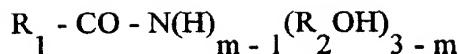
Betaine surfactants useful as suds boosters herein have the general formula:



wherein R is a hydrophobic group selected from alkyl groups containing from about 10 to about 22 carbon atoms, preferably from about 12 to about 18 carbon atoms, alkyl aryl and aryl alkyl groups containing a similar number of carbon atoms with a benzene ring being treated as equivalent to about 2 carbon atoms, and similar structures interrupted by amido or ether linkages; each R¹ is an alkyl group containing from 1 to about 3 carbon atoms; and R² is an alkylene group containing from 1 to about 6 carbon atoms.

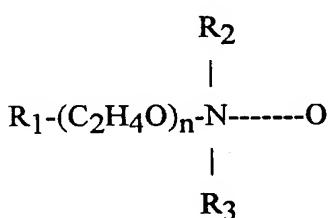
Examples of preferred betaines are dodecyl dimethyl betaine, cetyl dimethyl betaine, dodecyl amidopropyldimethyl betaine, tetradecyldimethyl betaine, tetradecylamidopropyldimethyl betaine, and dodecyldimethylammonium hexanoate. Other suitable amidoalkylbetaines are disclosed in U.S. Patent Nos. 3,950,417; 4,137,191; and 4,375,421; and British Patent GB No. 2,103,236, all of which are incorporated herein by reference.

Hydroxy-free amide surfactants useful as suds boosters herein include the ammonia, monoethanol, and diethanol amides of fatty acids having an acyl moiety containing from about 8 to about 18 carbon atoms. Such materials are characterized herein as "hydroxy-free" in order to distinguish them from the polyhydroxy fatty acid amides essentially used in the nonionic surfactant component hereinbefore described. Accordingly, "hydroxy-free" amides, for purposes of this invention, are those wherein the acyl moiety contains no hydroxy substituents. These materials are represented by the formula:

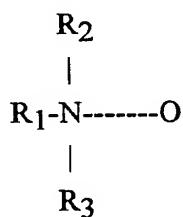


wherein R_1 is a saturated or unsaturated, hydroxy-free aliphatic hydrocarbon group having from about 7 to 21, preferably from about 11 to 17 carbon atoms; R_2 represents a methylene or ethylene group; and m is 1, 2, or 3, preferably 1. Specific examples of such amides are monoethanol amine coconut fatty acid amide and diethanolamine dodecyl fatty acid amide. These acyl moieties may be derived from naturally occurring glycerides, e.g., coconut oil, palm oil, soybean oil, and tallow, but can be derived synthetically, e.g., by the oxidation of petroleum or by hydrogenation of carbon monoxide by the Fischer-Tropsch process. The monoethanolamides and diethanolamides of C₁₂₋₁₄ fatty acids are preferred.

Amine oxide semi-polar nonionic surfactants useful as suds boosters/stabilizers comprise compounds and mixtures of compounds having the formula:

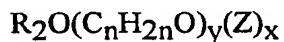


wherein R_1 is an alkyl, 2-hydroxyalkyl, 3-hydroxyalkyl, or 3-alkoxy-2-hydroxypropyl radical in which the alkyl and alkoxy, respectively, contain from about 8 to about 18 carbon atoms, R_2 and R_3 are each methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl, or 3-hydroxypropyl, and n is from 0 to about 10. Particularly preferred are amine oxides of the formula:



wherein R₁ is a C₁₂₋₁₆ alkyl and R₂ and R₃ are methyl or ethyl. The above hydroxy-free amides, and amine oxides are more fully described in U.S. Patent 4,316,824, incorporated herein by reference.

Other surfactants suitable for use as suds boosters/stabilizers in the compositions herein are the nonionic fatty alkylpolyglycosides. Such materials have the formula:



wherein Z is derived from glucose, R is a hydrophobic group selected from alkyl, alkylphenyl, hydroxyalkylphenyl, and mixtures thereof in which said alkyl groups contain from 8 to 22, preferably from 12 to 14 carbon atoms; n is 2 or 3 preferably 2, y is from 0 to 10, preferably 0; and x is from 1.5 to 8, preferably from 1.5 to 4, most preferably from 1.6 to 2.7. U.S Patents 4,393,203 and 4,732,704, incorporated herein by reference, describe these alkyl polyglycoside surfactants.

The suds booster/stabilizer component hereinbefore described must be present in the compositions herein in certain amounts relative to the nonionic surfactant component which has also been hereinbefore described. Thus, the total concentration of the nonionic surfactant component plus the suds booster/stabilizer component should be at least about 7%, preferably at least about 7%, of the compositions herein.

Aqueous Liquid Carrier

The light duty dishwashing detergent compositions herein further contain from about 40% to 60% of an aqueous liquid carrier in which the other essential and optional compositions components are dissolved, dispersed or suspended. More preferably the aqueous liquid carrier will comprise from about 45% to 55% of the compositions herein.

One essential component of the aqueous liquid carrier is, of course, water. The aqueous liquid carrier, however, may contain other materials which are liquid, or which dissolve in the liquid carrier, at room temperature and which may also serve some other function besides that of a simple filler. Such materials can include, for example, hydrotropes and solvents.

a) Hydrotropes

The aqueous liquid carrier may and preferably will comprise one or more materials which are hydrotropes. Hydrotropes suitable for use in the compositions herein include the C₁-C₃ alkyl aryl sulfonates, C₆-C₁₂ alkanols, C₁-C₆ carboxylic

sulfates and sulfonates, urea, C₁-C₆ hydrocarboxylates, C₁-C₄ carboxylates, C₂-C₄ organic diacids and mixtures of these hydrotrope materials.

Suitable C₁-C₃ alkyl aryl sulfonates include sodium, potassium, calcium and ammonium xylene sulfonates; sodium, potassium, calcium and ammonium toluene sulfonates; sodium, potassium, calcium and ammonium cumene sulfonates; and sodium, potassium, calcium and ammonium substituted or unsubstituted naphthalene sulfonates and mixtures thereof.

Suitable C₁-C₈ carboxylic sulfate or sulfonate salts are any water soluble salts or organic compounds comprising 1 to 8 carbon atoms (exclusive of substituent groups), which are substituted with sulfate or sulfonate and have at least one carboxylic group. The substituted organic compound may be cyclic, acyclic or aromatic, i.e. benzene derivatives. Preferred alkyl compounds have from 1 to 4 carbon atoms substituted with sulfate or sulfonate and have from 1 to 2 carboxylic groups. Examples of this type of hydrotrope include sulfosuccinate salts, sulfophthalic salts, sulfoacetic salts, m-sulfobenzoic acid salts and diester sulfosuccinates, preferably the sodium or potassium salts as disclosed in U.S. 3,915,903.

Suitable C₁-C₄ hydrocarboxylates and C₁-C₄ carboxylates for use herein include acetates and propionates and citrates. Suitable C₂-C₄ diacids for use herein include succinic, glutaric and adipic acids.

Other compounds which deliver hydrotropic effects suitable for use herein as a hydrotrope include C₆-C₁₂ alkanols and urea.

Preferred hydrotropes for use herein are sodium, potassium, calcium and ammonium cumene sulfonate; sodium, potassium, calcium and ammonium xylene sulfonate; sodium, potassium, calcium and ammonium toluene sulfonate and mixtures thereof. Most preferred are sodium cumene sulfonate and calcium xylene sulfonate and mixtures thereof. These preferred hydrotrope materials can be present in the composition to the extent of from about 3% to 8% by weight. Hydrotrope concentrations of about 4%-5% may be especially useful in imparting beneficial low temperature stability to the compositions herein.

b) Solvents

A variety of water-miscible liquids such as lower alkanols, diols, other polyols, ethers, amines, and the like may be used as part of the aqueous liquid carrier. Particularly preferred are the C₁-4 alkanols. Such solvents can be present in the compositions herein to the extent of from about 3% to 8%.

Optional Ingredients

Preferred optional ingredients in the dishwashing compositions herein include ancillary surfactants, calcium and/or magnesium ions, enzymes such as protease, and a stabilizing system for the enzymes. These and other optional ingredients are described as follows:

a) Ancillary Surfactants

The compositions herein may contain a wide variety of ancillary surfactants in addition to the essentially utilized surfactants hereinbefore described. Such ancillary surfactants, for example, can include C₈-22 alkyl sulfates; C₉-15 alkyl benzene sulfonates; C₈-22 olefin sulfonates; C₈-22 paraffin sulfonates; C₈-22 alkyl glyceryl ether sulfonates; fatty acid ester sulfonates; secondary alcohol sulfates; C₁₂-16 alkyl ethoxy carboxylates; C₁₁-16 secondary soaps; ampholytic detergent surfactants; and zwitterionic detergent surfactants.

b) Calcium and Magnesium Ions

The presence of both calcium and magnesium (divalent) ions can improve the cleaning of greasy soils for various compositions, i.e., compositions containing alkyl ethoxy sulfates and/or polyhydroxy fatty acid amides. This is especially true when the compositions are used in softened water that contains few divalent ions. It is believed that calcium and/or magnesium ions increase the packing of the surfactants at the oil/water interface, thereby reducing interfacial tension and improving grease cleaning.

Addition of both calcium and magnesium ions can also improve the low temperature stability of the compositions herein. This ion combination will thus preferably be present in the compositions herein at an active level of from about 0.2% to 2%, more preferably from about 0.3% to 1.5%, by weight.

Preferably, the magnesium ions are added as a hydroxide or as a chloride, sulfate, acetate, formate, oxide or nitrate salt to the compositions of the present invention. Inorganic salts such as chloride and sulfate are preferred and may provide an extra low temperature stability benefit. Such magnesium salts may comprise from about 2% to 6% of the compositions herein. Magnesium ions may also be added as the counterion to anionic surfactants that are employed. Calcium ions are preferably added to the compositions herein as salts of a hydrotrope.

The amount of calcium and magnesium ions present in compositions of the invention will be dependent upon the amount of total surfactant present therein. When calcium and magnesium ions are present in the compositions of this invention,

the molar ratio of calcium and magnesium ions to total anionic surfactant should be from about 0.25:1 to about 2:1.

Formulating such divalent ion-containing compositions in alkaline pH matrices may be difficult due to the incompatibility of the divalent ions, particularly magnesium, with hydroxide ions. When both divalent ions and alkaline pH are combined with the surfactant mixture of this invention, grease cleaning is achieved that is superior to that obtained by either alkaline pH or divalent ions alone. Yet, during storage, the stability of these compositions becomes poor due to the formation of hydroxide precipitates. Therefore, chelating agents discussed hereinafter may also be necessary.

c) Protease and/or Other Enzymes

The compositions of this invention can also optionally contain from about 0.001% to about 5%, more preferably from about 0.003% to about 4%, most preferably from about 0.005% to about 3%, by weight, of active protease, i.e., proteolytic, enzyme. Protease activity may be expressed in Anson units (AU.) per kilogram of detergent composition. Levels of from 0.01 to about 150, preferably from about 0.05 to about 80, most preferably from about 0.1 to about 40 AU. per kilogram have been found to be acceptable in compositions of the present invention.

Useful proteolytic enzymes can be of animal, vegetable or microorganism (preferred) origin. More preferred is serine proteolytic enzyme of bacterial origin. Purified or nonpurified forms of this enzyme may be used. Proteolytic enzymes produced by chemically or genetically modified mutants are included by definition, as are close structural enzyme variants. Particularly preferred is bacterial serine proteolytic enzyme obtained from *Bacillus subtilis* and/or *Bacillus licheniformis*.

Suitable proteolytic enzymes include Novo Industri A/S Alcalase® (preferred), Esperase®, Savinase® (Copenhagen, Denmark), Gist-brocades' Maxatase®, Maxacal® and Maxapem 15® (protein engineered Maxacal®) (Delft, Netherlands), and subtilisin BPN and BPN'(preferred), which are commercially available. Preferred proteolytic enzymes are also modified bacterial serine proteases, such as those made by Genencor International, Inc. (San Francisco, California) which are described in European Patent EP-B-251,446, granted December 28, 1994 and published January 7, 1988 (particularly pages 17, 24 and 98) and which are also called herein "Protease B". U.S. Patent 5,030,378, Venegas, issued July 9, 1991, refers to a modified bacterial serine proteolytic enzyme (Genencor International) which is called "Protease A" herein (same as BPN'). In particular see columns 2 and 3 of U.S. Patent 5,030,378 for a complete description, including amino sequence, of Protease A and

its variants. Preferred proteolytic enzymes, then, are selected from the group consisting of Alcalase® (Novo Industri A/S), BPN', Protease A and Protease B (Genencor), and mixtures thereof. Protease B is most preferred.

Another preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO 95/10615 published April 20, 1995 by Genencor International.

Useful proteases are also described in PCT publications: WO 95/30010 published November 9, 1995 by The Procter & Gamble Company; WO 95/30011 published November 9, 1995 by The Procter & Gamble Company; WO 95/29979 published November 9, 1995 by The Procter & Gamble Company.

Other optional enzymes such as lipase and/or amylase may be also added to the compositions of the present invention for additional cleaning benefits.

d) Enzyme Stabilizing System

The preferred compositions herein may additionally comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the protease or other enzymes used in the compositions herein. Such stabilizing systems can comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acid, boronic acid, polyhydroxyl compounds and mixtures thereof such as are described in U.S. Patents 4,261,868, Hora et al, issued April 14, 1981; 4,404,115, Tai, issued September 13, 1983; 4,318,818, Letton et al; 4,243,543, Guildert et al issued January 6, 1981; 4,462,922, Boskamp, issued July 31, 1984; 4,532,064, Boskamp, issued July 30, 1985; and 4,537,707, Severson Jr., issued August 27, 1985, all of which are incorporated herein by reference.

Additionally, from 0% to about 10%, preferably from about 0.01% to about 6% by weight, of chlorine bleach or oxygen bleach scavengers can be added to compositions of the present invention to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under

alkaline conditions. While chlorine levels in water may be small, typically in the range from about 0.5 ppm to about 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme during dishwashing is usually large; accordingly, enzyme stability in-use can be problematic.

Suitable chlorine scavenger anions are salts containing ammonium cations. These can be selected from the group consisting of reducing materials like sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc., antioxidants like carbonate, ascorbate, etc., organic amines such as ethylenediaminetetraacetic acid (EDTA) or alkali metal salt thereof and monoethanolamine (MEA), and mixtures thereof. Other conventional scavenging anions like sulfate, bisulfate, carbonate, bicarbonate, percarbonate, nitrate, chloride, borate, sodium perborate tetrahydrate, sodium perborate monohydrate, percarbonate, phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc. and mixtures thereof can also be used.

e) Miscellaneous Optional Ingredients

Other conventional optional ingredients which are usually used in additive levels of below about 5% include opacifiers, antioxidants, bactericides, dyes, thickeners (e.g., hydroxypropyl methylcellulose), perfumes, and the like. Furthermore, detergency builders can also be present in the compositions herein in amounts of from 0% to about 50%, preferably from about 2% to about 30%, most preferably from about 5% to about 15%. It is typical in light-duty liquid or gel dishwashing detergent compositions to have no detergent builder present. However, certain compositions containing magnesium or calcium ions may require the additional presence of low levels of, preferably from 0 to about 10%, more preferably from about 0.5% to about 3%, chelating agents selected from the group consisting of bicine/bis(2-ethanol)blycine), citrate N-(2-hydroxyethyl) iminodiacetic acid (HIDA), N-(2,3-dihydroxy- propyl) diethanolamine, 1,2-diamino-2-propanol N,N'-tetramethyl-1,3-diamino-2-propanol, N,N-bis(2-hydroxyethyl)glycine (a.k.a. bicine), and N-tris(hydroxymethyl)methyl glycine (a.k.a. tricine) are also preferred. Mixtures of any of the above are acceptable.

Thickened Products

Liquid dishwashing detergent compositions of this invention which are relatively thick, i.e., which have higher viscosity, can be prepared without the use of polymeric thickeners by selecting specific types and amounts of the components

hereinbefore described. In particular, relatively thickened products can be realized by:

- 1) keeping the nonionic surfactant component substantially free, i.e., containing no more than 1% by weight of the composition, of polyhydroxy fatty acid amide material;
- 2) keeping the calcium ion concentration in the composition at 0.35% or less;
- 3) keeping the magnesium ion concentration in the composition at 0.75% or less;
- 4) using no more than 3% by weight of the composition of C₁-₄ alkanols in the aqueous liquid carrier; and
- 5) using from about 4% to 8% by weight of the composition of a hydrotrope selected from xylene and toluene sulfonates.

The liquid detergent compositions of the instant invention that are thickened will have a Brookfield viscosity of from about 500 to 3,500 cps at 25°C. More preferably, such thickened products will have a viscosity of from about 800 to 2,000 cps at 25°C. For purposes of this invention, viscosity is measured with a Brookfield LVTDV-11 viscometer apparatus using an RV#2 spindle at 1.0 rpm.

Composition pH

The dishwashing compositions of the present invention will generally provide a 10% aqueous solution pH of from about 6 to 8. More preferably, the compositions herein will be alkaline in nature with a 10% aqueous solution pH of from about 7 to 7.8. Compositions of especially desirable low temperature stability may be realized by keeping the 10% aqueous solution pH of the products herein below about 7.5.

Dishwashing compositions of the invention will be subjected to acidic stresses created by food soils when put to use, i.e., diluted and applied to soiled dishes. If a composition with a pH greater than 7 is to be more effective, it should contain a buffering agent capable of providing a generally more alkaline pH in the composition and in dilute solutions, i.e., about 0.1% to 0.4% by weight aqueous solution, of the composition. The pKa value of this buffering agent should be about 0.5 to 1.0 pH

units below the desired pH value of the composition (determined as described above). Preferably, the pKa of the buffering agent should be from about 7 to about 9.5. Under these conditions the buffering agent most effectively controls the pH while using the least amount thereof.

The buffering agent may be an active detergent in its own right, or it may be a low molecular weight, organic or inorganic material that is used in this composition solely for maintaining an alkaline pH. Preferred buffering agents for compositions of this invention are nitrogen-containing materials. Some examples are amino acids or lower alcohol amines like mono-, di-, and tri-ethanolamine. Useful inorganic buffers/alkalinity sources include the alkali metal carbonates, e.g., sodium carbonate.

The buffering agent, if used, is present in the compositions of the invention herein at a level of from about 0.1% to 15%, preferably from about 1% to 10%, most preferably from about 2% to 8%, by weight of the composition.

Composition Preparation

The liquid or gel dishwashing detergent compositions herein may be prepared by combining the essential and optional ingredients together in any convenient order using suitable agitation to form a homogeneous product. Preferred methods for making detergent compositions of the type disclosed herein, and for preparing various components of such compositions, are described in greater detail in Ofosu-Asante; U.S. 5,474,710; Issued December 12, 1995, incorporated herein by reference.

Composition Stability

The liquid dishwashing detergent products of the present invention exhibit desirable phase stability when subjected to prolonged low temperature and freeze/thaw testing. For example, when products are exposed to 40°F (4.4°C) temperature conditions and inspected for evidence of phase instability such as haziness, the compositions of the present invention are generally stable for not less than 4 days. When such products are subjected to freezing conditions, 0°F (-18°C) for 16 hours, and then heated, the temperature at which they recover from phase instability caused by freezing should be 60°F (16°C) or lower.

Dishwashing Method

Soiled dishes can be contacted with an effective amount, typically from about 0.5 ml. to about 20 ml. (per 25 dishes being treated), preferably from about 3 ml. to about 10 ml., of the detergent composition of the present invention. The actual

amount of liquid detergent composition used will be based on the judgment of user, and will typically depend upon factors such as the particular product formulation of the composition, including the concentration of active ingredient in the composition, the number of soiled dishes to be cleaned, the degree of soiling on the dishes, and the like. The particular product formulation, in turn, will depend upon a number of factors, such as the intended market (i.e., U.S., Europe, Japan, etc.) for the composition product. The following are examples of typical methods in which the detergent compositions of the present invention may be used to clean dishes. These examples are for illustrative purposes and are not intended to be limiting.

In a typical U.S. application, from about 3 ml. to about 15 ml., preferably from about 5 ml. to about 10 ml. of a liquid detergent composition is combined with from about 1,000 ml. to about 10,000 ml., more typically from about 3,000 ml. to about 5,000 ml. of water in a sink having a volumetric capacity in the range of from about 5,000 ml. to about 20,000 ml., more typically from about 10,000 ml. to about 15,000 ml. The detergent composition has a surfactant mixture concentration of from about 21% to about 44% by weight, preferably from about 25% to about 40% by weight. The soiled dishes are immersed in the sink containing the detergent composition and water, where they are cleaned by contacting the soiled surface of the dish with a cloth, sponge, or similar article. The cloth, sponge, or similar article may be immersed in the detergent composition and water mixture prior to being contacted with the dish surface, and is typically contacted with the dish surface for a period of time ranging from about 1 to about 10 seconds, although the actual time will vary with each application and user. The contacting of the cloth, sponge, or similar article to the dish surface is preferably accompanied by a concurrent scrubbing of the dish surface.

In a typical European market application, from about 3 ml. to about 15 ml., preferably from about 3 ml. to about 10 ml. of a liquid detergent composition is combined with from about 1,000 ml. to about 10,000 ml., more typically from about 3,000 ml. to about 5,000 ml. of water in a sink having a volumetric capacity in the range of from about 5,000 ml. to about 20,000 ml., more typically from about 10,000 ml. to about 15,000 ml. The detergent composition has a surfactant mixture concentration of from about 20% to about 50% by weight, preferably from about 30% to about 40%, by weight. The soiled dishes are immersed in the sink containing the detergent composition and water, where they are cleaned by contacting the soiled surface of the dish with a cloth, sponge, or similar article. The cloth, sponge, or similar article may be immersed in the detergent composition and water mixture prior to being contacted with the dish surface, and is typically contacted with the dish

surface for a period of time ranging from about 1 to about 10 seconds, although the actual time will vary with each application and user. The contacting of the cloth, sponge, or similar article to the dish surface is preferably accompanied by a concurrent scrubbing of the dish surface.

In a typical Latin American market application, from about 1 ml. to about 50 ml., preferably from about 2 ml. to about 10 ml. of a detergent composition is combined with from about 50 ml. to about 2,000 ml., more typically from about 100 ml. to about 1,000 ml. of water in a bowl having a volumetric capacity in the range of from about 500 ml. to about 5,000 ml., more typically from about 500 ml. to about 2,000 ml. The detergent composition has a surfactant mixture concentration of from about 5% to about 40% by weight, preferably from about 10% to about 30% by weight. The soiled dishes are cleaned by contacting the soiled surface of the dish with a cloth, sponge, or similar article. The cloth, sponge, or similar article may be immersed in the detergent composition and water mixture prior to being contacted with the dish surface, and is typically contacted with the dish surface for a period of time ranging from about 1 to about 10 seconds, although the actual time will vary with each application and user. The contacting of the cloth, sponge, or similar article to the dish surface is preferably accompanied by a concurrent scrubbing of the dish surface.

Another dishwashing method used worldwide involves direct application of the detergent compositions herein, either neat or diluted in a dispenser bottle, onto the soiled dishes to be cleaned. This can be accomplished by using a device for absorbing liquid dishwashing detergent, such as a sponge or dishrag, which is placed directly into a separate quantity of undiluted or somewhat diluted liquid dishwashing composition for a period of time typically ranging from about 1 to about 5 seconds. The absorbing device, and consequently the undiluted or somewhat diluted liquid dishwashing composition, can then be contacted individually with the surface of each of the soiled dishes to remove food soil. The absorbing device is typically contacted with each dish surface for a period of time ranging from about 1 to about 10 seconds, although the actual time of application will be dependent upon factors such as the degree of soiling of the dish. The contacting of the absorbing device with the dish surface is preferably accompanied by concurrent scrubbing. Prior to contact and scrubbing, this method may involve immersing the soiled dishes into a water bath without any liquid dishwashing detergent. After scrubbing, the dish can be rinsed under running water.

The following Examples illustrate the invention and facilitate its understanding.

EXAMPLES I-IV

Light-duty liquid dishwashing detergent products having the following compositions are prepared:

<u>Ingredient</u>	<u>Concentration</u> (Wt.%)			
	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>
Sodium C ₁₂₋₁₃ alkyl ethoxy (1.4) sulfate	36	--	--	--
Sodium C ₁₂₋₁₃ alkyl ethoxy (1.0) sulfate	--	36	--	34.4
Sodium C ₁₂₋₁₃ alkyl ethoxy (0.6) sulfate	--	--	34	--
C ₁₂₋₁₄ glucose amide	1.5	1.5	1.5	--
Coconut amine oxide	5.2	5.2	4.9	8.0
EO/PO block co-polymer - Tetronic® 704	0.4	0.4	0.4	0.4
Neodol® C ₁₁ E ₉ alcohol ethoxylate	1.0	1.0	1.0	--
Ethanol	5.3	5.3	5.6	6.5
Calcium xylene sulfonate	3.0	3.2	3.6	--
Sodium xylene sulfonate	1.2	1.2	1.4	5.4
Magnesium chloride	2.8	2.8	2.8	2.4
Water and minors	---Balance to 100%---			
pH (10% solution)	7.4	7.4	7.4	7.7

These liquid dishwashing detergent products all provide excellent greasy soil removal from dishes and excellent sudsing when they are used in aqueous dishwashing solution to clean dirty dishware. These products also have especially desirable low temperature stability as evidenced, for example, by their performance under 40°F (4.4°C) Constant Temperature conditions and their clarity recovery from 0°F (-18°C) freeze/thaw testing.

EXAMPLE V

A thickened, light-duty liquid dishwashing detergent product of relatively high viscosity is prepared having the following formula: This product is free of polyhydroxy fatty acid amides and polymeric thickeners.

EXAMPLE V

<u>Ingredient</u>	<u>Concentration (Wt%)</u>
Sodium C ₁₂ -13 alkyl ethoxy (1.0) sulfate	37
Coconut amine oxide	5
EO/PO block co-polymer - Tetronic®704	0.4
Neodol® C ₁₁ E ₉ alcohol ethoxylate	1.0
Ethanol	1.5
Sodium xylene sulfonate	4.1
Calcium xylene sulfonate	1.6
Mg ⁺⁺	0.3
Water and minors	----Balance to 100%---
pH (10% solution)	7.5
Viscosity (cps)	1020

What is claimed is:

1. An aqueous, light duty liquid detergent composition which has especially desirable low temperature stability and which also has especially desirable greasy soil removal and sudsing performance when used to clean soiled dishware, said composition characterized by:
 - A) from 34 % to 40% by weight of an anionic surfactant component which is characterized by slightly ethoxylated alkyl ether sulfates containing from about 8 to 18 carbon atoms in the alkyl group and from 0.4 to 1.6 moles of ethylene oxide per molecule;
 - B) from 0.3% to 4.5% by weight of a nonionic surfactant component which is characterized by surfactants selected from the group consisting of C₈₋₁₈ polyhydroxy fatty acid amides, C₈₋₁₈ alcohol ethoxylates having from 1 to 15 moles of ethylene oxide, ethylene oxide-propylene oxide block copolymer surfactants and combinations of said nonionic surfactants;
 - C) from 4.5% to 9% by weight of a suds booster/stabilizer selected from the group consisting of betaine surfactants, hydroxy-free fatty acid amides, amine oxide semipolar nonionic surfactants, C₈₋₂₂ alkylpolyglycosides and combinations of said suds boosters/stabilizers; with the proviso that within said composition the total concentration of this suds booster/stabilizer Component C and said nonionic surfactant Component B is at least 7% by weight; and
 - D) from 40% to 60% by weight of an aqueous liquid carrier.
2. An aqueous, light duty liquid detergent composition which has especially desirable low temperature stability and which also has especially desirable greasy soil removal and sudsing performance when used to clean soiled dishware, said composition characterized by:
 - A) from 35 % to 38% by weight of an anionic surfactant component which is characterized by slightly ethoxylated alkyl ether sulfates containing from 11 to 14 carbon atoms in the alkyl group and from 0.5 to 1.4 moles of ethylene oxide per molecule;

- B) from 0.4% to 4.0% by weight of a nonionic surfactant component which is characterized by surfactants selected from the group consisting of C₁₁-14 polyhydroxy fatty acid amides, C₁₁-14 alcohol ethoxylates having from about 6 to 12 moles of ethylene oxide, ethylene oxide-propylene oxide block copolymer surfactants and combinations of said nonionic surfactants;
- C) from 5.0% to 9% by weight of a suds booster/stabilizer selected from the group consisting of betaine surfactants, amine oxide semipolar nonionic surfactants, and combinations of said suds boosters/stabilizers; with the proviso that within said composition the total concentration of this suds booster/stabilizer Component C and said nonionic surfactant Component B is at least 9% by weight;
- D) from 0.2% to 2% by weight of the combination of both Mg⁺⁺ and Ca⁺⁺ ions; and
- E) from 40% to 60% by weight of an aqueous liquid carrier.

3. A composition according to Claims 1-6 which has a 10% aqueous solution pH of 7.5 or less.

4. A composition according to Claims 1-7 which contains at least 5% by weight of the composition of a hydrotrope selected from alkali metal and calcium xylene and toluene sulfonates.

5. A composition according to Claims 1-8 wherein the composition contains no more than 1% by weight of an ethoxylated alcohol nonionic surfactant.

6. A composition according to Claims 1-9 wherein the source of magnesium ions is magnesium chloride or magnesium sulfate.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 98/11813

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C11D 1/83, C11D 1/29

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, CLAIMS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9520027 A1 (THE PROCTER & GAMBLE COMPANY), 27 July 1995 (27.07.95), see the whole document --	1-6
X	WO 9405758 A1 (THE PROCTER & GAMBLE COMPANY), 17 March 1994 (17.03.94), see the whole document --	1-6
X	WO 9206161 A1 (THE PROCTER & GAMBLE COMPANY), 16 April 1992 (16.04.92), see page 10, line 14 - line 22; page 13, line 26 - page 18, line 35; claims --	1-6

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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SA 96329

INTERNATIONAL SEARCH REPORT

Information on patent family members

27/07/98

International application No.

PCT/US 98/11813

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